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# Heavy Metals in Agricultural Lands Receiving Chemical Sewage Sludges

Volume IV

Research Report No. 51



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Research Program for the Abatement of Municipal Pollution  
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These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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HEAVY METALS IN AGRICULTURAL  
LANDS RECEIVING CHEMICAL SEWAGE SLUDGES

VOLUME IV

(Analytical Methods for Sewage Sludge Analysis)

by

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Institute for Environmental Studies  
University of Toronto

RESEARCH PROGRAM FOR THE ABATEMENT  
OF MUNICIPAL POLLUTION WITHIN THE  
PROVISIONS OF THE CANADA-ONTARIO  
AGREEMENT ON GREAT LAKES WATER QUALITY

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## ABSTRACT

This report reviews existing and newly developed analytical methods for sewage sludge analysis. It had been stressed earlier that knowledge of the form of metals in waste and environmental samples is of great importance. As a result of this the development of simple equipment and analytical methods to initiate metal speciation has been stressed.

Procedures developed earlier and used provisionally have been studied in depth. The mercury method is now acceptable as recorded. The As/Se procedure has been modified as a result of further investigation. Nonflame atomic absorption methods have been developed for silver and vanadium.

It is demonstrated that using atomic absorption spectroscopy as a detector does not guarantee a quick solution to metal speciation problems.

Sludges can be dry-ashed at 450<sup>0</sup>C without fear of loss of cadmium, lead or appreciable amounts of zinc. When aluminum is to be determined, dry-ashing should not be used. Data also make it clear that incineration at temperatures usually employed will release large amounts of arsenic, cadmium, lead, mercury and zinc.

A number of sewage sludges were analyzed, and the results are tabulated.

## RÉSUMÉ

Le présent rapport examine les méthodes classiques et nouvelles d'analyser les boues résiduaires. On a déjà souligné le grand intérêt qu'il y a à connaître la forme que revêtent les métaux présents dans les échantillons de déchets ou ceux prélevés dans l'environnement; on a donc fait un grand effort pour mettre au point des méthodes d'analyse et des appareils simples.

Les méthodes définies antérieurement et utilisées depuis on fait l'objet d'une étude exhaustive. Le procédé d'analyse s'appliquant au mercure est maintenant acceptable sans modification. Toutefois, après un examen approfondi, on a modifié celui qui sert à déceler l'arsenic et le sélénium. On a mis au point des méthodes d'absorption atomique sans flamme s'appliquant à l'argent et au vanadium.

Il est démontré que la spectroscopie d'absorption atomique ne permet pas nécessairement de spécifier rapidement les métaux.

Les boues peuvent s'incinérer à 450° C sans provoquer de perte de cadmium, de plomb ou de quantités mesurables de zinc. Par contre, lorsqu'on est en présence d'aluminium, il faut éviter l'incinération. Les observations démontrent finalement que l'incinération aux températures normalement employées libère des quantités considérables d'arsenic, de cadmium, de plomb, de mercure et de zinc.

Un certain nombre d'échantillons de boues résiduaires ont fait l'objet d'analyses et les résultats sont présentés sous forme de tableau.

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## INTRODUCTION

As agreed to in the past two years, the work during this contract interval centred on studies into methods for the chemical analysis of sludge. At this time it is apparent that knowing the form of metals in wastes and environmental samples is of great importance. Hence, following the start made last year, a proportionately larger effort was spent on developing simple equipment and methods to initiate metal speciation studies.

Existing procedures, labelled "provisional" in last year's report, were studied in depth. The As/Se procedure has been modified as a result of this work, but the mercury method is acceptable as recorded.

Some environmentally important metals, e.g., silver (Ag), vanadium (V) and tin (Sn) are not readily analyzed in sludges by conventional flame atomic absorption. Nonflame atomic absorption methods were developed for Ag and V. The hydride method for Sn was investigated extensively, but more work remains to be done before satisfactory results can be reported.

It is clear that obtaining total heavy metal data on wastes and environmental samples does not necessarily allow a meaningful interpretation of the environmental impact of the metals. This is particularly evident in a number of published studies on lead (Pb) and mercury (Hg). Other metals have been studied with a much reduced effort to date. It is likely, as is already becoming evident in the case of cadmium (Cd), that metal speciation will be of great importance in in-depth investigations of most metals in the environment.

Work in this laboratory and in a few others suggests that combining atomic absorption as a detector with powerful separational techniques is a relatively simple and inexpensive method of doing metal speciation work. This is particularly true when working with complex samples like sludge. Atomic absorption is a specific detector for the metal being analyzed. This should make results more easily interpreted than those obtained with comparably priced, less selective, detectors presently available.

Metal speciation studies are much more difficult than studies involving total heavy metals. As will be seen below, using atomic absorption spectroscopy as a detector does not guarantee a quick solution to metal speciation problems. However, it is this author's opinion that atomic absorption spectroscopy will, in time, make as great a contribution to metal speciation studies as it did in the past decade to the routine analysis of total metals.

## NONFLAME ATOMIC ABSORPTION METHOD FOR VANADIUM

Of the metals not presently being analyzed in sludges, V is probably of greatest interest environmentally. The nitrous oxide acetylene flame method for V does not have a low enough detection limit to be useful for the analysis of many sludges. Even worse, it has been our experience that the flame method gives erroneously high values near the detection limit (10  $\mu\text{g/g}$ ). For example, a sludge which by other methods had a value of 13  $\mu\text{g/g}$  persistently gave 20  $\mu\text{g/g}$  by flame atomic absorption.

The flameless atomic absorption determination of V has been studied by a few researchers, e.g., Everett and West (1) and Chakrabarti and Hall (2) in lubricating oils, Jackson et al (3) in titanium dioxide ( $\text{TiO}_2$ ) and Cioni et al (4) in silicate rocks. Jackson et al (3) reported that a wide range of elements and  $\text{H}_2\text{SO}_4$  depress the V signal. Cioni et al (4) found an enhancement from titanium (Ti) and aluminum (Al) when present as the chlorides.

2.1 Experimental2.1.1 Instrumental conditions chosen

Using the Perkin Elmer 303 and HGA 2000 the following conditions were found to be optimum:

Absorbing Line		3184 $^{\circ}\text{A}$
Background Correction		Deuterium Arc ( $\text{D}_2$ arc)
Slit		7 $\text{\AA}$
Dry	100 $^{\circ}\text{C}$	30 sec
Ash	1200 $^{\circ}\text{C}$	30 sec
Atomize	Max Temp	23 sec

2.1.2 Recommended method

The sample is dissolved as recommended by Van Loon et al (5). The instrument is allowed to warm up for at least 20 minutes to stabilize the  $\text{D}_2$  arc. The  $\text{D}_2$  arc and V lamp beams are carefully aligned.

Samples are analyzed by the method of standard additions. Three solutions are used, the sample by itself and then two aliquots of the sample spiked with an appropriate concentration of dilute V standard solution (usually sample + 0.2 to 0.8  $\mu\text{g}/\text{ml}$  V). Fifty  $\mu\text{l}$  aliquots of these solutions are placed separately in the furnace and run using the conditions listed above.

#### 2.1.3 Interference study

It was necessary to investigate interferences because authors who had previously made comprehensive interference studies used the Carbon Rod analyzer rather than the graphite tube. Table 1 lists the results of this study for some of the elements expected to cause problems. Fifty  $\mu\text{l}$  of 0.5  $\mu\text{g}/\text{ml}$  V solution was mixed with 1000  $\mu\text{g}/\text{ml}$  of the potential interferent. Several of the interference effects noted are different from those reported by other authors, but in any case the pattern is complex, and hence the method of standard additions should probably be used.

In proposing the method of standard additions it is important to ascertain that the calibration curve is linear over the range of concentrations being used. This was investigated for a number of sludges using the sample and at least 3 aliquots which were spiked. In all cases a linear calibration curve (using peak height measurement) was indicated up to a total concentration of about 2  $\mu\text{g}/\text{ml}$  V.

Nonspecific background problems were noted, particularly when working near the detection limit. Hence the  $\text{D}_2$  arc was used.

#### 2.1.4 Investigation of instrumental parameters

The atomizing temperature and time duration of atomizing cycle are the most critical of the instrumental parameters. It is very important to atomize at maximum temperature ( $\sim 2700^{\circ}\text{C}$ ) for a time interval sufficient to minimize memory effects. It is important to watch the peak shape to be certain that the sample has been fully atomized. If incomplete atomization is indicated (pen does not return to baseline during the atomization cycle), the maximum temperature button should be activated until the pen returns to the base line.

TABLE 1. VANADIUM INTERFERENCE STUDY

<u>Concomitant</u>	<u>Absorbance</u>
none	0.100
Cu(NO <sub>3</sub> ) <sub>2</sub>	0.088
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.057
Fe(C1)	0.088
Mg(C1)	0.088
Na(C1)	0.088
K(C1)	0.100
Zn(C1)	0.100
Si(NO <sub>3</sub> ) <sub>2</sub> *	0.094
Al(C1)	0.083
HNO <sub>3</sub> (6N)	0.063
HCl (6N)	0.088

\*Si was 100  $\mu\text{g}/\text{ml}$

## 2.2 Results

The proposed procedure was tested on a Kodak standard reference material, TEG-50, NBS standard fly ash and standard Canada Centre for Inland Waters (CCIW) sludges D and F. In the case of the last samples, no data were supplied by CCIW; hence the "accepted" value given was obtained by using neutron activation and solvent extraction/flame atomic absorption.

TABLE 2. VANADIUM RESULTS BY THE PROPOSED PROCEDURE ( $\mu\text{g}/\text{g}$ )

	<u>Obtained</u>		<u>Accepted</u>
	$\bar{x}$	$s_{\bar{x}}$	
TEG 50	50	3	50
NBS fly ash	220	10	214
Sludge F	15	2	13
Sludge D	25	2	32

These results are in acceptable agreement with the values for the standards. The detection limit for the method is 1-2  $\mu\text{g}/\text{g}$  in sludge.

Silver has been shown to be highly toxic to simple life forms, such as algae. Hence it could be an important metal to be studied in sludges.

In previous reports flame atomic absorption was used for the analysis of silver. Unfortunately, Ag levels in many sludges are near the detection limit for this method. Nonspecific background interference problems, as recorded by Minkkinen (6), are large and sometimes difficult to correct. Nonflame atomic absorption has been shown to give better detection limits for Ag in samples high in organic matter. Sludges contain a matrix high in inorganic or organic materials. The following study was carried out to see if Ag in sludges could be better analyzed by nonflame atomic absorption.

### 3.1 Experimental

#### 3.1.1 Instrumental conditions chosen

Using the Perkin Elmer 303 fitted with the HGA 2000 furnace the following conditions were found to be optimum:

Absorbing Line	3281 $\text{\AA}$	
Background correction	Deuterium arc and/or 3324 $\text{\AA}$	$\text{\AA}$
		nonabsorbing line (see discussion below)
Slit	7 $\text{\AA}$	
Dry	100 $^{\circ}\text{C}$	30 sec
Ash	1000 $^{\circ}\text{C}$	30 sec
Atomize	2600 $^{\circ}\text{C}$	8 sec

#### 3.1.2 Recommended method

Dissolve the sample as recommended by Van Loon et al (5). Ag levels vary widely in sludges and hence the dilution required must be found experimentally. The best working range using 50  $\mu\text{l}$  samples was found to be 2-25  $\mu\text{g/l}$  in the sample solution.

The instrument is allowed to warm up for at least 20 minutes to stabilize the D<sub>2</sub> arc. The D<sub>2</sub> arc and Ag lamp beams are very carefully aligned.

Five to fifty  $\mu$ l aliquots of standard and sample solutions are pipetted separately into the furnace. The thermal program is activated. A standard curve is produced by reading peak heights of standards. Unknowns (sludges) are read off the standard curve.

As indicated below, the background corrector gives error signals from time to time. The nonabsorbing line method must be used in these cases as follows.

Find the nonabsorbing line at 3324  $\text{\AA}$ . Run the samples under the same conditions as for the absorbing line. Subtract the background signal thus obtained.

### 3.1.3 Discussion on method of composition

Chloride can cause low values of Ag due to precipitation of Ag in the sample solution as AgCl. Present experience suggests that sludges contain some chloride salts so it is important not to add more by using an acid containing chlorine. A simple decomposition using nitric acid will suffice to release over 90% of the Ag present in the sludges tested.

### 3.1.4 Atomization temperature

Silver begins to be volatilized from the furnace at 1200 $^{\circ}$ C. However, atomization is incomplete at temperatures up to 2000 $^{\circ}$ C. Best peak heights were obtained at 2600 $^{\circ}$ C. Because of the aforementioned losses at 1200 $^{\circ}$ C, charring must be done below this temperature.

### 3.1.5 Interference problems

Section 4 of this report on background correction should be noted carefully. The deuterium arc background corrector may give erroneous corrections, as explained in this section. Nonspecific background absorption was found to be very high, in the region of the 3281  $\text{\AA}$  resonance line for Ag. It is important to be certain that the corrector is properly aligned and working within its proper range.

It was found that 50  $\mu$ l of 1000 ppm of Ag free Al, Na, K and Ca as nitrates gave absorbances, even when the background corrector

was on, corresponding to up to 3  $\mu\text{g/g}$  Ag in sludges. When errors of this type are experienced it is recommended that background correction be made using the 3324 Å nonabsorbing line.

No appreciable chemical interferences were noted for elements present in sludge sample solutions.

### 3.2 Results

Three reference samples were analyzed by the flameless method and the results are given in Table 3.

TABLE 3. SILVER ( $\mu\text{g/g}$ )

<u>Sample</u>	<u>Ag Found</u>		<u>Ag "accepted"</u>
	$\bar{x}$	$s_x$	
Kodak TEG-50	50	2	46
CCIW Sludge D	48	4	50*
CCIW Sludge F	3	1	2.2*

\*Values obtained by neutron activation analysis (7)

These results are in acceptable agreement with the values obtained by other workers using other methods. The detection limit for Ag in sludge is 0.1 - 0.5  $\mu\text{g/g}$ .

#### 3.2.1 Application of the method to sewage liquids

The above method can be used on the liquid fraction of sewage. A fresh sample is filtered through 0.45  $\mu$  porosity membrane filters. Directly inject 50 ml of the filtrate into the furnace and run as above.

Brantford sewage liquid averaged 7  $\mu\text{g/l}$  Ag using this procedure.

## PROBLEMS EXPERIENCED WITH BACKGROUND CORRECTION

Nonspecific (background) interference results from absorption by molecules or by scattering of incident radiation in the region of the resonance line. The magnitude and nature of this problem depends very critically on the position of the optical beam in the flame and on flame composition. Hence, continuum background correction systems must be optically aligned with the hollow cathode beam. In addition, if the nonabsorbing line method is used the flame conditions must be kept identical for measurements at the resonance and nonabsorbing lines.

Over the years serious problems in analyzing sludge sample solutions have been experienced using both the nonabsorbing line and continuum background correction systems. The following are recommendations based on a study done this year.

### 4.1 Nonabsorbing Line Method

Before continuum background corrector systems were generally available Van Loon et al (5) recommended a number of nonabsorbing lines which could be used for background correction. These have been generally very satisfactory for background correction purposes, in some cases being better than using the continuum source for a few elements. However, problems can occur:

1. Some of the recommended lines may be too weak or may not be present in newer lamps or lamps made by other manufacturers.
2. Using some sample solutions the background absorption can slope strongly in the region of the resonance line, thus requiring the use of two nonabsorbing lines, one on either side of the resonance line.

In general, it is advisable to use a continuum background corrector when such a device is applicable.

### 4.2 Continuum Background Correction Method

There are a number of continuum background correction systems available commercially. These are normally deuterium or hydrogen lamps. In one recent introduction a tungsten lamp has been made available to

cover wavelengths above 3200  $\text{\AA}$  where the intensity of even the deuterium arc has fallen sharply.

A number of problems exist when using continuum background correction:

1. The intensity of hydrogen lamps, and often even deuterium sources, is too low using the recommended slit width to allow for a balancing of continuum and resonance line signals. Using equipment in this laboratory it has been impossible for the reason given above to use continuum background correction for the analysis of nickel in sludge sample solutions.
2. The intensity of continuum sources falls sharply above 3200  $\text{\AA}$ . Contrary to popular belief it is sometimes necessary to correct for nonspecific absorption effects at wavelengths longer than this. For elements such as Cu, Ag and Cr the nonabsorbing line method must often be used.
3. It is crucially important to have the beams from the background correction system and the resonance line optically coincident. This can often be done visually for systems with reflective optics. The manufacturers recommendations should be read and followed closely.
4. Continuum background correctors fail to operate properly when the background absorbance exceeds a certain value. On some systems it is impossible to know when this has happened. Error signals are produced which often cannot be distinguished from true signals. In general background correctors fail to work when background levels exceed 0.7 to 1 absorbance units. It may be necessary to check the magnitude of the background using a nonabsorbing line before proceeding to use continuum background correction.

#### 4.3        Flame versus Nonflame Background

The lower concentration elements in sludges are often now being analyzed by nonflame atomic absorption. Background problems are much greater for nonflame methods. For this reason it is important to be aware of the details in section 3.2. The present author has experienced great difficulties with background correction during sludge analyses and it is hoped that other workers may benefit from his problems.

## INVESTIGATIONS INTO THE HYDRIDE TECHNIQUE

As indicated in last year's report, work was continuing on the provisional procedure proposed for As and Se. The following adjustments to the procedure should be made to ensure good results.

5.1 Waiting Period Prior to the Injection of Hydride Vapours into Absorption Cell

For many sample types, e.g. sludge and orchard leaves, with complex matrices, it is important to swirl the mixture contained in the syringe for 15 seconds prior to injecting the hydrides into the absorption cell. This should be done in the manner indicated in the revised procedure given below.

5.2 Strength of Sodium Borohydride

A 2% solution of sodium borohydride was found to be better than the 1% recommended previously. This helps to assure that other elements present, which may consume borohydride, do not interfere with the production of the As or Se hydrides.

5.3 Sample Decomposition

No recommendation on sample decomposition was made in last year's report. However, after further investigation, two approaches have been found to be worth recommending.

An acid decomposition with 5 ml  $\text{HNO}_3$ , 1 ml  $\text{H}_2\text{SO}_4$  and 0.5 g  $\text{K}_2\text{S}_2\text{O}_8$  for a 0.1 g sample can be used. Add 5 ml concentrated HCl for a 50 ml dilution. It is important to evaporate the mixture toward the end of the decomposition period until nitrogen oxides have been expelled. The presence of more than a trace quantity of nitrogen oxides severely depresses the absorbance obtained subsequently.

It is also possible to use a KOH fusion decomposition. Five to eight pellets of KOH are added to 0.1 g of sample in a nickel crucible. The fusion is accomplished at dull red heat. Concentrated  $\text{H}_2\text{SO}_4$  is added slowly to the fusion until the alkali has just been neutralized. One ml excess  $\text{H}_2\text{SO}_4$  and three ml water are added. The sample is filtered through Whatman #42 paper into a 50 ml flask and diluted to volume with water. (HCl added?)

5.4 Modified Procedure for Hydride Generation

With the syringe plunger firmly depressed, insert the needle into a standard or sample solution. (Sample must be cool - room temperature). Suck up 5 cc of solution. Wipe any drops from the needle. Insert the needle into the 2% sodium borohydride solution and withdraw the plunger to upper black line (2 oz mark). Quickly invert the syringe. Wipe away any liquid on the needle tip. Hold a tissue over the tip swirl for 15 seconds.\* Insert the needle into the plastic tubing at a point three inches from the inlet to the absorption cell. Press zero button. Press integrate button (integration is set for 2 seconds). Immediately, with the other hand, depress the plunger of the syringe. Injection is stopped just prior to the liquid reaching the needle. The injection period should coincide with the 2 second integration and end at the termination of the integration period. This step takes some practice but acceptable reproducibility can be obtained after a short period of time. Blanks must also be run.

---

\*The underlined section is the modification of the provisional procedure given in last year's report.

In last year's report a quartz "T" tube was described for use with atomic absorption spectroscopy which separated the volatilizer from the atomizer section. Using this device it is possible to selectively volatilize metal compounds during a heating program and detect their presence in the separate atomizer. The atomizer need not be a quartz tube, as in the diagram following, but could be a flame or a graphite furnace, depending on the metal being studied. The volatilizer section has been designed to accommodate a gas chromatographic column to allow study of compounds of Hg, Pb, Se and As. Experimental work using gas chromatography indicated that design changes of the "T" tube, described in last year's report, should be made. The new tube is described in detail in the section below.

### 6.1 Experimental

A Perkin Elmer 305B atomic absorption unit with deuterium arc background corrector was used. Hollow cathodes used were recent models available from Westinghouse.

#### 6.1.1 Furnace

The quartz "T" tube furnace is shown in Figures 1A and 1B.

The volatilization section is 20 cm long by 4.5 cm I.D. narrowing to an 8 cm long 8 mm I.D. neck which connects to the atomizer. The atomizer is 10 cm long by 2 cm I.D. The gas inlet tubes in the neck and on the male part of the ground glass joint are of any convenient size. The volatilization and atomizer sections are wound with size 20 chromel c wire, 0.65 ohm/foot. Asbestos insulation is used to cover the windings to a 1 cm thickness. The furnaces are powered by ordinary laboratory variacs. A temperature of 900 to 1000°<sup>o</sup>C is commonly used in the atomizer.

Hydrogen gas is injected into the atomizer using the gas inlet quartz tube closest to the atomizer. This tube runs inside the neck to a point five mm inside the atomizer. The hydrogen flow rate is about one l/min.

The nitrogen inlet tube, the other quartz tube on the volatilizer neck, opens directly into the neck. Nitrogen flow is

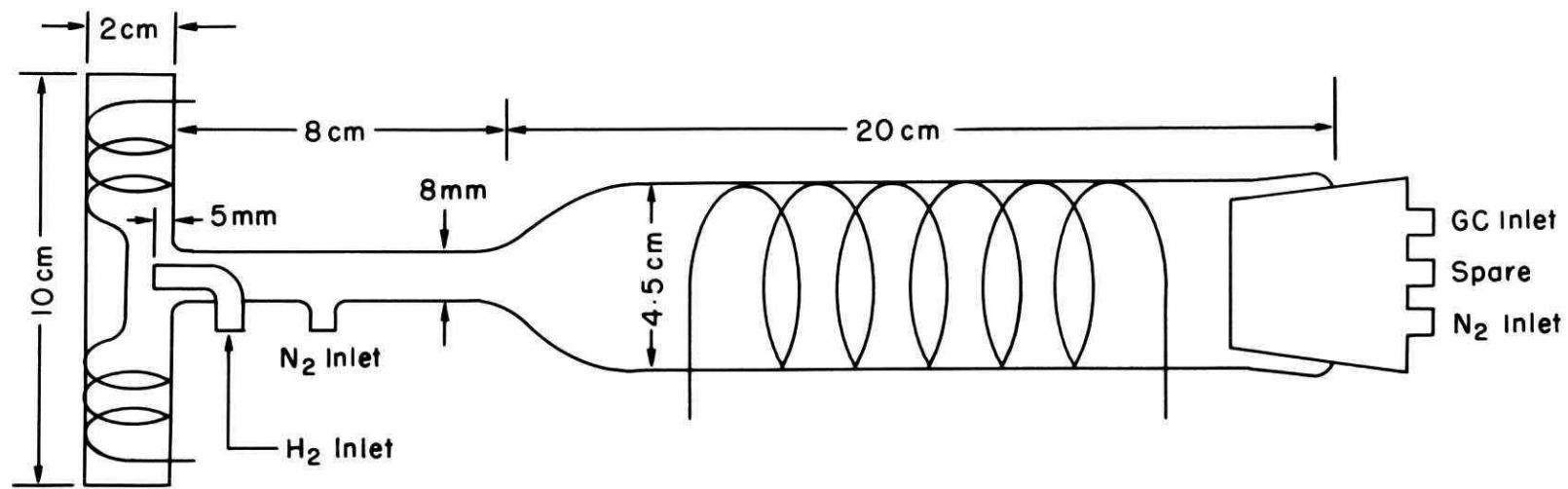


FIGURE 1A. SCHEMATIC OF QUARTZ "T" TUBE

commonly six l/min using any inlet tube in the male part of the glass joint.

#### 6.1.2 Gas chromatographic apparatus

The columns were constructed by Chromatographic Specialties, Brockville, Ontario, in a helix wound form. The smallest diameter which could be wound without causing flattening, and hence obstruction of the flow, was 4 cm. The column was prepared from a 122 cm length of 3 mm I.D. Al tubing. A length of empty Al tube was left on both ends of the column. One end was long enough to reach five mm inside the atomizer. The other extended to just outside the volatilization chamber.

Column packings can be as required for a particular purpose. In the present work, with Se, a 20% polymetaphenylether (five ring) on 60/80 mesh chromabsorb w was found to be suitable. This column is stable to 250°C.

The inlet valve from a Beckmann GC-2 was used. Heating tape was wound around the section of the inlet valve tubing outlet, outside the volatilizer, connecting to the gas chromatographic column. Swagelock fittings can be used as connectors.

Carrier gas flow rate ( $N_2$ ) in the column ranged from 8 to 30 ml/min depending on the application.

Columns were cured for several hours at 200°C with the carrier gas on.

#### 6.1.3 Temperature and absorbance recording

A Sargent Welch Model DSRG double pen recorder was used. One channel was connected to a Pt/Rh thermocouple and cold reference junction. The other channel monitored the atomic absorption signal, in absorbance.

#### 6.1.4 Reagents

Reagents were obtained from Alfa Products Ltd., Beverley, Massachusetts. The Se organics, dimethyl-, diethyl-, and dimethyldiselenide were shipped as liquids sealed in ampoules. Working standards of the Se compounds were prepared by diluting to an appropriate level in 95% ethanol.

### 6.1.5 Atomizer alignment

Place the "T" tube atomizer on the burner as in Figure 2. While monitoring the hollow cathode lamp beam, move the atomizer up and down, in and out, with the burner adjustment screws until minimum absorbance is noted.

## 6.2 Methods

### 6.2.1 Selective volatilization from solids or liquids

Turn on atomizer and allow to warm up (20 min.). Turn on atomic absorption unit, deuterium arc and recorder. Set the instrument parameters according to the manufacturer's instructions. Make certain that the deuterium arc beam is properly aligned with the hollow cathode beam. Place the wet sludge sample into the centre of the volatilizer. While placing the male section of the ground glass joint in place make certain that the thermocouple is close to or touching the sample. Begin the  $N_2$  flow from the inlet in the male section of the ground glass joint at six l/min. After 10-20 seconds, turn on the  $H_2$  flow into the atomizer at one l/min. Zero the atomic absorption unit. Begin the temperature program and monitor temperature and absorbance.

### 6.2.2 Gas chromatography

Set up the atomic absorption unit as outlined above. Allow furnaces and inlet valve to reach the desired temperature. Turn on the  $N_2$  purge at six l/min and  $N_2$  carrier gas through the column at the desired rate. Begin the  $H_2$  flow into the atomizer at one l/min. Insert the thermocouple so the tip rests on the column. Be certain that the column temperature has been stabilized. Using  $\mu$ l syringe with a fine needle insert the desired volume of sample as a liquid or gas into the inlet valve. Rinse the pipet with 95% ethanol and with the next sample to be run.

### 6.2.3 Procedural and equipment discussion

Temperature Calibration: The thermocouple was placed in a suitable sample of known melting point in the volatilizer. Using the method for selective volatilization, the temperature is increased until melting occurs. At this point a sudden aberration is noted on the temperature record. In addition, an absorbance signal is commonly

recorded as a significant vapour pressure of the compound occurs. Several compounds of known melting point, covering the temperature range of interest, can be run.

Choice of Atomizer: There is an increasing environmental interest in the elements Se and As. Resonance lines for these elements are in the region of the UV below 2000 Å. The quartz tube atomizer with an H<sub>2</sub> diffusion flame was found to be the best type of atomizer for this application. Other environmentally interesting elements such as Pb, Cd and Hg are readily atomized in this device. If higher atomization temperatures are desired, the volatilization chamber can be interfaced with a flame.

The volatilization chamber can also be interfaced, using a Ta transfer tube, with an HGA 2000 furnace. For the elements tested no advantage in this arrangement could be found.

Volatilization Chamber: Workers who possess a graphite furnace, e.g., the HGA 2000 or 2100, can use this for selective volatilization studies. However, this device cannot be used for gas chromatography and is expensive if not already available. Temperatures attainable are much greater and hence studies of compounds with much less volatility are possible.

### 6.3 Results

#### 6.3.1 Selective volatilization

Some procedures for sludge analysis contain steps involving heating periods at elevated temperature. According to the literature in other fields, metals such as Hg, As, Cd, Pb and Zn can be lost if the temperature used exceeds certain generally accepted levels. For example, it is generally accepted from work on biological materials that samples containing Hg should be heated at temperatures below 80°C during drying processes to avoid losses. Selective volatilization work done last year and continued this year shows that appreciable Hg is not lost from sludges tested at temperatures below 125°C. This means that the drying period for sludge can be reduced considerably by using a higher temperature.

Losses of Pb, Cd, Zn and As were studied at temperatures up to 950°C. This study provides data which are helpful in establishing

maximum temperatures at which sludges can be dry-ashed or incinerated without loss of the metals. It will help in the identification of the metal species responsible for the loss.

6.3.1.1 Lead. Figure 3 is included as a typical example of an output display obtained during selective volatilization. It is interesting to note the relatively flat absorbance baseline up to about 560°C where the majority of the lead begins to be volatilized. This means not only is no appreciable lead lost at lower temperatures, but also no other volatilized materials (e.g. H<sub>2</sub>O, organics, other metals) are detected to confuse the picture. This latter point is most important because it illustrates the high degree of specificity exhibited by atomic absorption spectroscopy even when dealing with complex samples such as sewage sludge. Because of this, the proposed technique is very simple to use, freeing the researcher from the confusion usually associated with the interpretation of complicated output obtained by most competitive techniques.

The compound of Pb being lost is likely PbCl<sub>2</sub> (mpt 501°C). When low Pb sludges were "salted" with PbCl<sub>2</sub> a similar chart to Figure 2 was obtained. This helps to substantiate the conclusion mentioned above.

6.3.1.2 Cadmium. Heating studies of Cd volatilization show that in most sludges no loss of Cd occurs below 480°C. For a few sludges losses were not detected until 550°C. No compound could be postulated from present data as the cause of Cd loss.

6.3.1.3 Zinc. Most Zn in the sludges tested by the thermal volatilization procedure was lost beginning at about 460°C. However, in a few cases, small peaks were obtained at about 270°C; these peaks do not represent more than 1-2% of the total Zn. As with cadmium it is not yet possible to speculate as to the compounds causing Zn losses.

6.3.1.4 Arsenic. Heat volatility loss of As in sludges begins at about 340°C. Evidence to date suggests that this loss may be due to As<sub>2</sub>O<sub>3</sub>.

#### 6.4 Discussion

It is still too early in this research to be certain about the identity of the lead and arsenic compounds postulated above. However,

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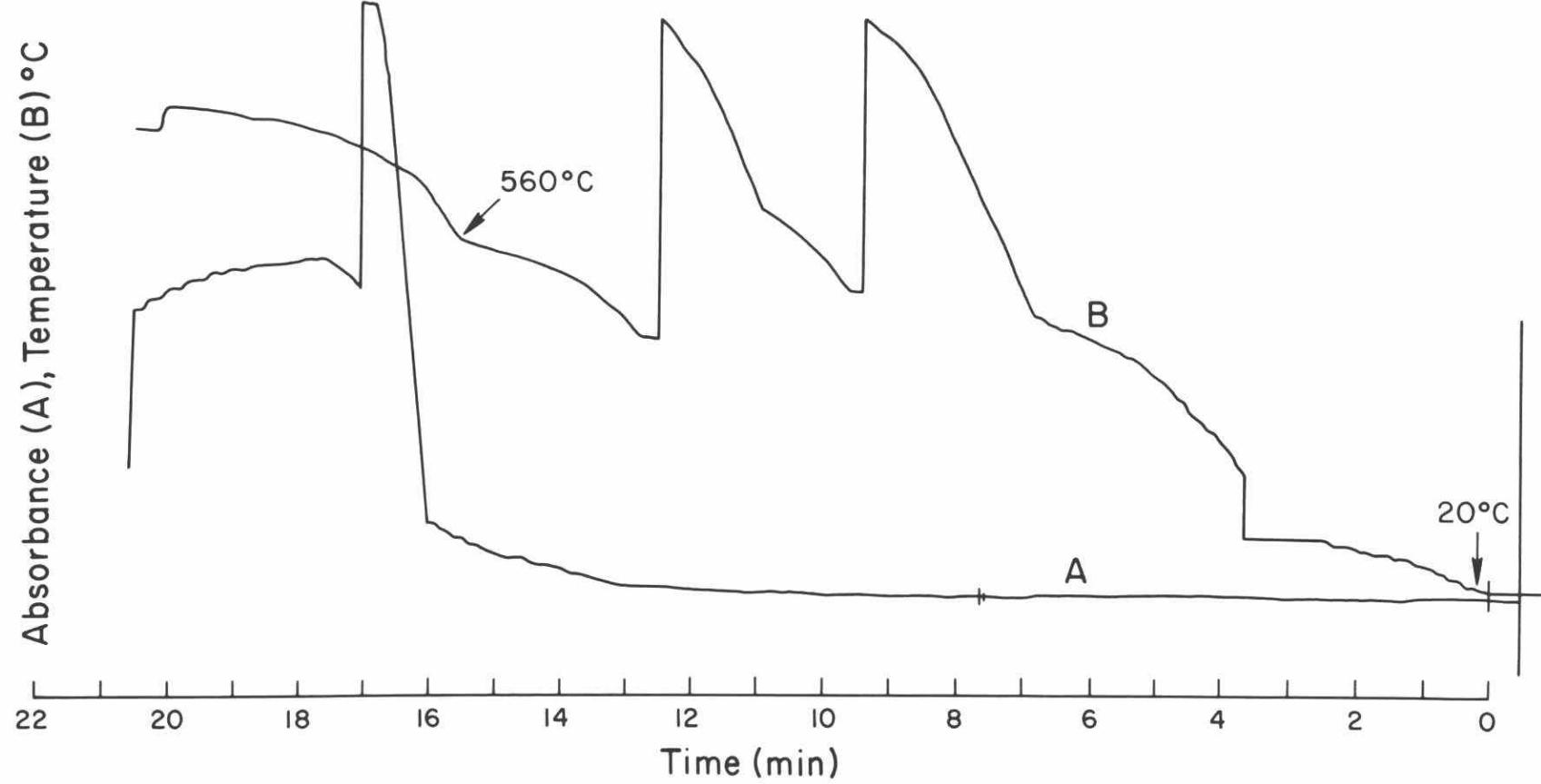


FIGURE 3. GRAPH ILLUSTRATING OUTPUT OBTAINED FOR THE VOLATILITY OF LEAD

using atomic absorption spectroscopy as a detector for volatilization studies has given data much more simple to interpret than could be obtained by competitive techniques.

Peaks obtained for most metal losses were broad, suggesting that more than one compound might be responsible for volatilization. It is important to modify the above procedure in a way that will allow this possibility to be studied.

#### 6.5 Conclusions

It is evident from this work that sludges can be dry-ashed at 450°C without fear of loss of Cd, Pb or appreciable Zn. When As is to be determined, dry-ashing should not be employed. The temperature of 450°C has been used by workers in the past, but without direct evidence (actually detecting metal in the vapour) for dry-ashing sludges. These data also make it clear that incineration at the temperatures usually employed will release large amounts of Cd, Zn, As, Hg and Pb.

## 7. GAS CHROMATOGRAPHY INVESTIGATION

To evaluate initially the capabilities of the gas chromatography/atomic absorption system it was necessary to have a supply of volatile metal organic standards. Selenium alkanes were readily available.

Ten  $\mu$ l samples of a mixture of 0.05% quantities of the three Se alkanes were injected into the inlet valve using  $T_c$  82°C,  $T_i$  180°C and an  $N_2$  flow rate of 23 l/min. A typical chromatogram obtained is shown in Figure 4A. The detection limit for standards by this method is 10 ng dimethylselenide, 20 ng diethylselenide and 20 ng dimethyldiselenide (Figures 4B and C).

Gases released by *astragalus racemosus* were trapped in a silicone oil DC 550 on 60/80 mesh chromabsorb W, precolumn and then released into the gas chromatograph by heating. By this technique dimethylselenide was found to be present in the transpiration gases in addition to the previously reported dimethyldiselenide.

The procedure was applied to ethanol and cyclohexane extracts of sewage sludge. No peaks were obtained. This suggests that no low boiling point Se compounds are present in sludges at detection limits of this procedure (10 ng dimethyl-, 20 ng diethyl- and 20 ng dimethyldiselenide).

Work is presently being done on Pb and Hg. Extracts of sludge are placed into the injection valve as above. To date an evaluation of experimental conditions has not been completed. Early evidence suggests that there are no low boiling point Pb compounds, which result is consistent with thermal volatilization studies.

Work is continuing with Pb, As and Hg.

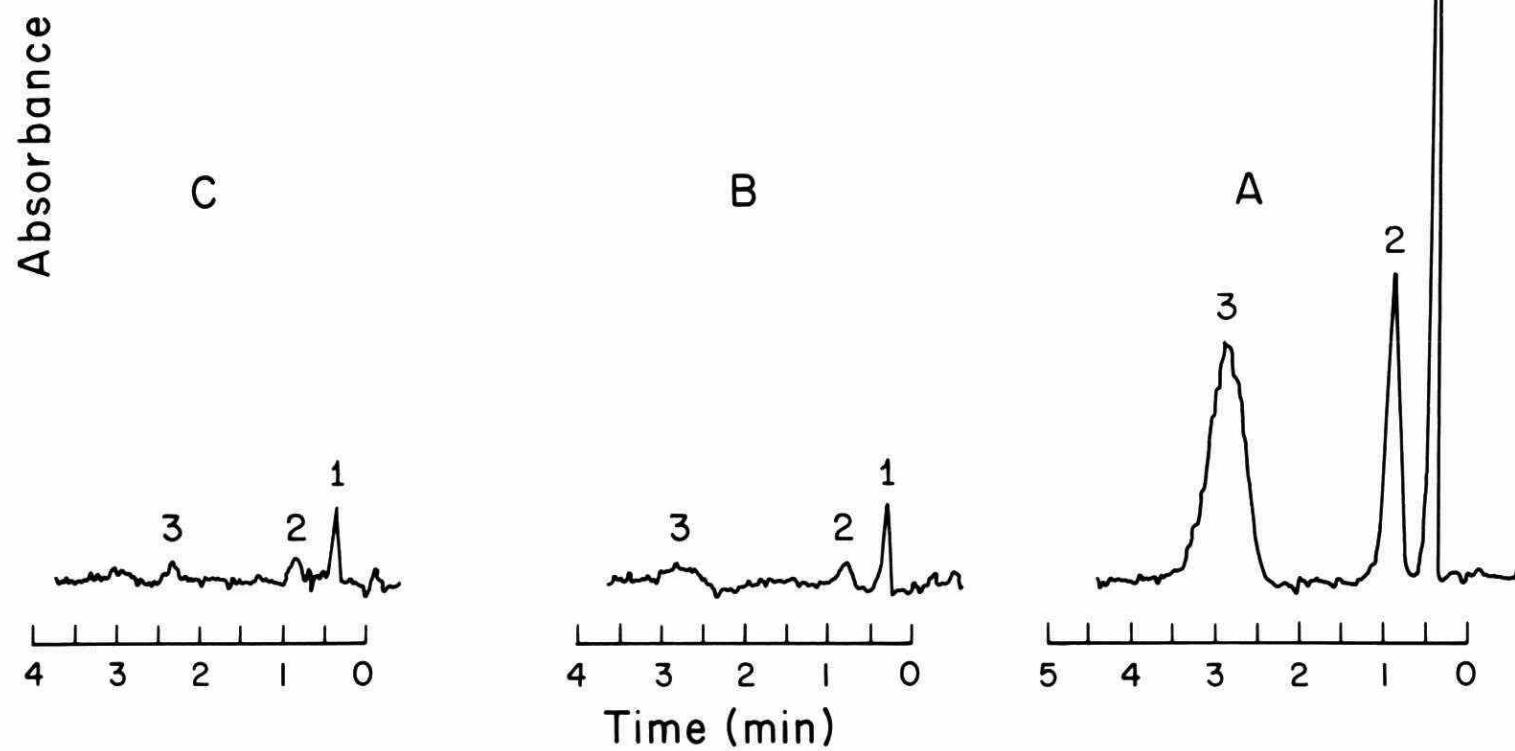


FIGURE 4. CHROMATOGRAMS OF Se ALKANES, PEAK 1 DIMETHYLDISELENIDE, PEAK 2 DIETHYLDISELENIDE AND PEAK 3 DIMETHYLDISELENIDE

## 8. LIQUID CHROMATOGRAPHY/ATOMIC ABSORPTION STUDIES

To complement the above work liquid chromatography/atomic absorption studies (Figure 5) have recently been initiated. This technique can be used with liquid extracts of sludges and provides the same high degree of specificity to metal compound identification as gas chromatography/atomic absorption.

The interfacing used in this laboratory is very simple, as is shown in Figure 5. Effluent from the column is aspirated by a direct connection into the nubulizer capillary.

Most work to date has been done using ion exchange resins in an attempt to determine the various valence states of Cu, Fe and As present in sludges. It is too early to arrive at any conclusions.

### 8.1 Discussion

Although little quantitative metal speciation data have yet been obtained, this laboratory is now in a unique position to investigate metal speciation in sludges. The tools have now been developed and are in an advanced stage of evaluation. It is obvious, even at this early point, that the combination of atomic absorption as a metal specific detector with separational techniques is the most exciting concept proposed to date for metal speciation in complex environmental samples. Work using this type of equipment is relatively simple and most inexpensive compared to conventional equipment formerly used for this work. It is hoped that this laboratory can obtain funding to carry on with the research.

## 9. RESULTS OBTAINED ON CCIW SLUDGES USING DIFFERENT DECOMPOSITION METHODS

In October, 1975, Ross Knechtel of the Canada Centre for Inland Waters circulated Table XXIII of the Sewage Sludge Round Robin Study. This table is entitled "Proposed Composition of Samples A, B, D and F." Data in this table represent analyses done mainly by atomic absorption spectroscopy but also in a few instances by x-ray fluorescence spectroscopy and neutron activation methods. This is the first time that standard sewage sludges have been available on which to test procedures. It is of interest to try a number of different acid decomposition methods to see the agreement obtained compared to these CCIW values. Concentrated acids are used in each case.

### 9.1 Methods

#### 9.1.1 Method 1

Weigh 0.2 g sample into a 100 ml beaker. Dissolve using a mixture of 4 ml  $\text{HNO}_3$  and 12 ml HCl. Heat for one hour on medium heat of a hot plate. Add one ml  $\text{HNO}_3$  and ten ml  $\text{H}_2\text{O}$ . Warm for five minutes and filter into a 25 ml flask. Make dilutions as required.

#### 9.1.2 Method 2

Weigh 0.2 g sample into a 100 ml beaker. Add ten ml  $\text{HNO}_3$  and evaporate on medium heat to near dryness. Add ten ml  $\text{HNO}_3$  and two ml  $\text{HClO}_4$  and evaporate to dryness on medium heat. Add one ml  $\text{HNO}_3$  and ten ml  $\text{H}_2\text{O}$ , warm, and then filter into a 25 ml flask. Make appropriate dilutions as required.

#### 9.1.3 Method 3

Weigh 0.2 g sample into a teflon dish. Add ten ml  $\text{HNO}_3$  and ten ml HF. Evaporate to dryness on medium heat. Add ten ml  $\text{HNO}_3$ , transfer the sample to a 100 ml beaker and add two ml  $\text{HClO}_4$ . Evaporate to dryness on medium heat. Add one ml  $\text{HNO}_3$  and ten ml  $\text{H}_2\text{O}$  and warm. Filter into a 25 ml flask. Make appropriate dilutions.

### 9.2 Results

The results obtained for the standard sludges are given in Table 4.

TABLE 4. METALS IN CCIW SLUDGES BY DIFFERENT  
DECOMPOSITION METHODS

Method and Sample	Fe	Al	Zn	Cu	Ni	Pb μg/g	Cd	Mn	Cr
A 1	0.5	0.2	690	150	10	110	2.6	230	20
2	0.5	0.2	750	130	12	110	2.6	260	20
3	0.8	1.0	750	120	30	120	2.6	270	37
Acc*	0.6	0.2	735	135	7.4	101	2.1	242	26
B 1	6.5	1.7	2,500	1,200	28	1,000	16	390	390
2	6.5	1.7	2,560	1,200	28	1,000	17	395	330
3	6.6	2.7	2,600	1,200	28	1,100	17	440	370
Acc	7.6	1.8	2,700	1,300	28	1,000	19	399	391
D 1	7.3	0.8	9,000	770	28	2,950	80	2,200	130
2	7.4	0.9	9,500	770	28	2,950	85	2,300	130
3	7.6	2.3	9,200	770	35	3,000	80	2,400	130
Acc	9.3	1.1	10,400	780	33	3,100	90	2,500	160
F 1	5.3	1.3	850	630	22	550	6.7	390	90
2	5.3	1.6	860	640	28	550	5.1	400	90
3	5.6	1.9	850	640	35	550	4.6	400	100
Acc	5.6	1.4	927	650	21	560	5.3	407	115

\*Acc = Value from CCIW Table XXIII

In most instances, the methods yield results which are in acceptable agreement with the CCIW values. However, in the case of Zn low values are obtained, particularly by the  $\text{HNO}_3/\text{HCl}$  method. For Al the HF method gives values which are much higher than the CCIW value, due probably to the release of silicate bound Al. Except for sample F, the Fe results obtained by all methods are persistently lower than CCIW values.

Despite these several problems this writer does not feel that a change in decomposition methods is warranted unless, for some reason, a total decomposition is required. In sludge studies researchers are not often interested in very tightly bound metal. Any metal which is

not released by an  $\text{HNO}_3/\text{HCl}$  decomposition is not likely to be released into the environment in a harmful manner. Methods involving use of HF and  $\text{HClO}_4$  require special equipment and precautions. They should not be used routinely, if data obtained by ordinary mineral acids is suitable.

## 10. PLASMA EMISSION SPECTROSCOPY

Commercial instrumentation has become available recently for plasma emission spectroscopy (\$50,000 to \$80,000). Claims for the technique include multielement capability, superior detection limits to atomic absorption, cheaper prices compared to a per element analysis by atomic absorption spectroscopy and precision and accuracy comparable to atomic absorption spectroscopy.

With these claims in mind, sewage sludges D and F were sent as blind standards in a group of samples for plasma emission analysis to a reputable commercial laboratory. The results obtained are listed in Table 5 and compared with results from CCIW Table XXIII of the Sewage Sludge Round Robin study.

TABLE 5. PLASMA EMISSION ANALYSIS OF SLUDGES (μg/g)

	<u>Sludge D</u>		<u>Sludge F</u>	
	Plasma	CCIW	Plasma	CCIW
Mg	3950	9300	2740	5500
Mn	1570	2500	278	407
Ni	23	32	15	21
Na	4920	688	566	894
Al	8060	10700	13100	14100
Cd	68	90	7	5.3
Cu	595	868	506	656
Fe	41800	98500	8330	63400
Zn	9910	10400	467	927
Cr	133	163	74	115
Pb*	2580	3100	525	557

\*Pb done by atomic absorption

The writer believes that plasma emission has great promise for the future. However, at this early stage one must proceed with extreme caution in using these results.

## 11. ROUTINE CHEMICAL ANALYSIS OF SLUDGE FOR METALS

Only the Brantford sewage treatment plant supplied samples for analysis this year. Table 6 gives the results obtained. Each sample represents a composite obtained from the digester over a two-week period. Samples were dried at 110°C.

TABLE 6. BRANTFORD 1975 ANALYSES

Wt %	As	Hg	Cd	Mn	Cr	Ni	% ppm					
							Pb	Zn	Cu	Al	Fe	
B1	3	1	2	17	240	730	110	0.12	0.27	0.12	0.43	5.5
B2	5	2	2	17	230	730	110	0.11	0.23	0.14	0.39	5.7
B3	6	1	3	16	220	720	100	0.11	0.21	0.13	0.41	5.8
B4	6	1	3	18	240	730	85	0.11	0.21	0.12	0.44	8.2
B5	4	1	4	18	450	450	145	0.15	0.22	0.14	0.48	8.1
B6	3	2	4	19	280	600	135	0.13	0.46	0.13	0.48	7.0
B7	5	2	4	20	300	530	85	0.12	0.23	0.11	0.69	6.1
B8	4	1	3	21	240	590	90	0.13	0.27	0.11	0.46	6.3
B9	4	1	3	25	210	550	105	0.12	0.27	0.12	0.48	6.5
B10	5	1	3	23	200	510	90	0.10	0.23	0.10	0.49	7.4
B11	4	2	4	15	410	610	150	0.11	0.28	0.13	0.43	5.8
B12	3	2	3	13	370	520	145	0.09	0.29	0.11	0.46	5.0
B13	4	2	4	16	350	610	130	0.10	0.32	0.11	0.48	5.3

CCIW standard sludges D and F were used as control samples.

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